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(71) Applicants
Matsushita Electric Industrial Company Limited, No. 1006 Oaza Kadoma, Kadoma City, Osaka, Japan
(72) Inventors
Masaru Ikedo, Yoshitake Yasuno, Osamu Yamamoto
(74) Agents
J. A. Kemp & Co

(54) Electrooptic ceramic material

(57) A transparent and electrooptic ferroelectric ceramic material comprises the composition

$$(Pb_{1-x}A_aB_b)(Zr_yTi_{1-y})_{1-\frac{x}{4}}O_3,$$

where A represents a rare earth element such as Nd, Sm, Eu, Gd or La, B represents a Group I, II or III element such as Li, Na, K, Mg, Sr, Ba or Al, $0.04 \leq x \leq 0.15$, $0.6 \leq y \leq 0.8$, $a+b = x$, $a \neq 0$ and $b \neq 0$. This ceramic material is superior in electrooptic effect to conventional lead lanthanum zirconate titanate ceramics and can easily be produced in desired shapes and sizes by hot-pressing.

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Fig. 1

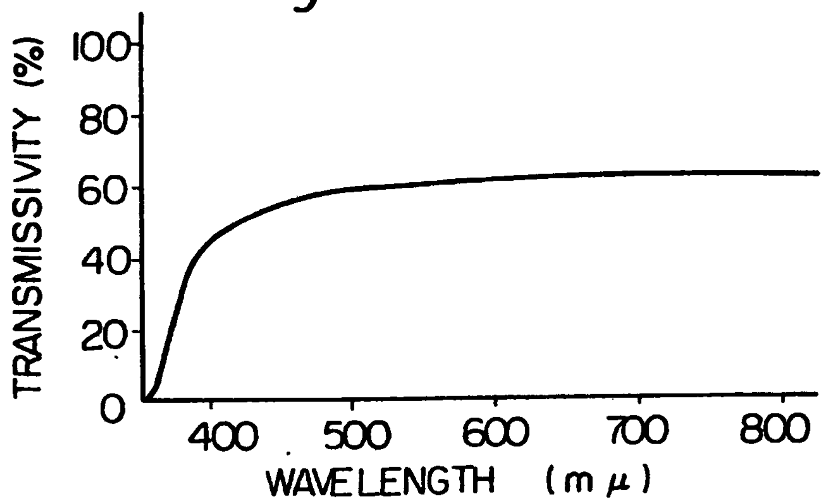
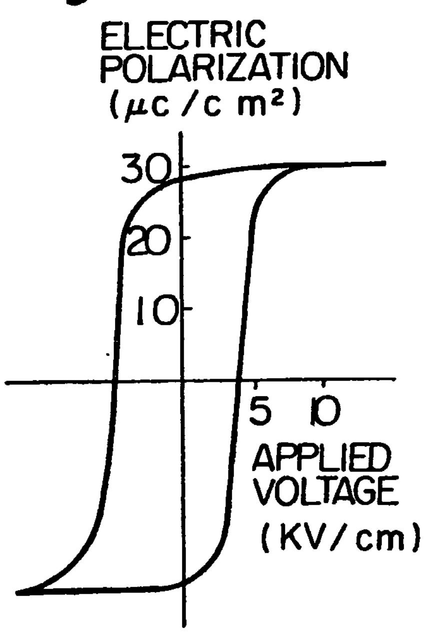
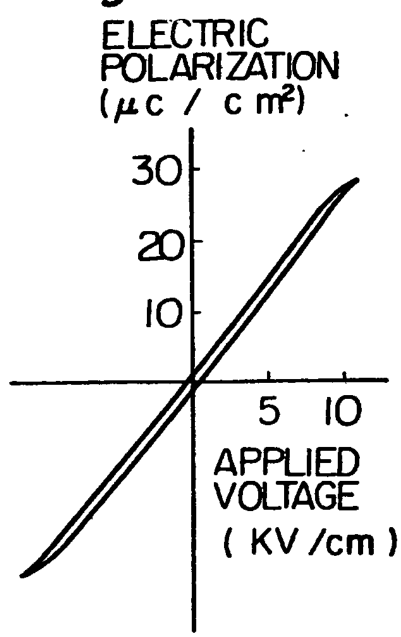


Fig. 2



(WIDE TYPE)

Fig. 3



(SLIM TYPE)

Fig. 4

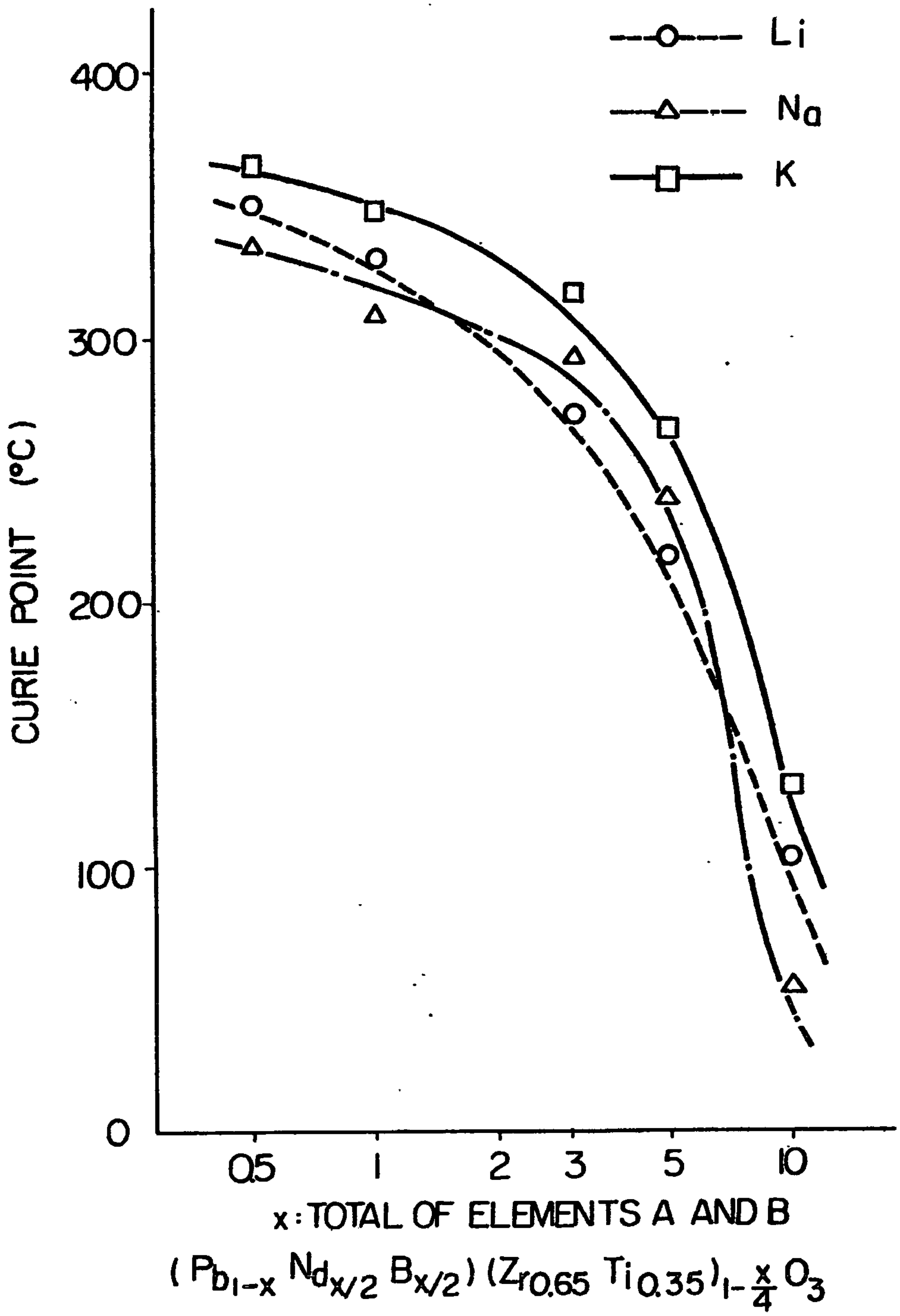

Li
Na
K
CURIE POINT (°C)
400
300
200
100
0
0.5
1
2
3
5
10
x : TOTAL OF ELEMENTS A AND B
$(Pb_{1-x}Nd_{x/2}B_{x/2})(Zr_{0.65}Ti_{0.35})_{1-\frac{x}{4}}O_3$

Fig. 5

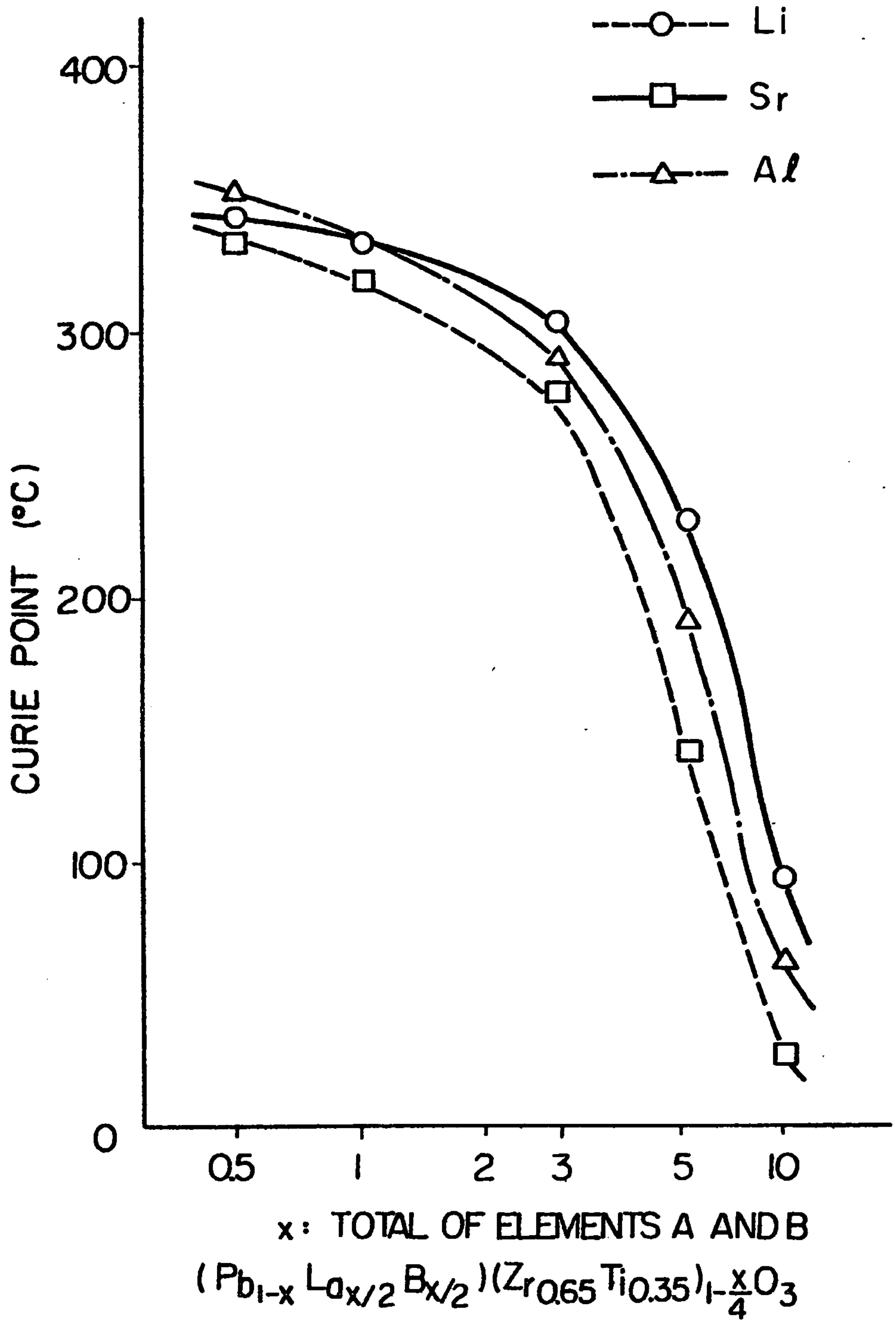
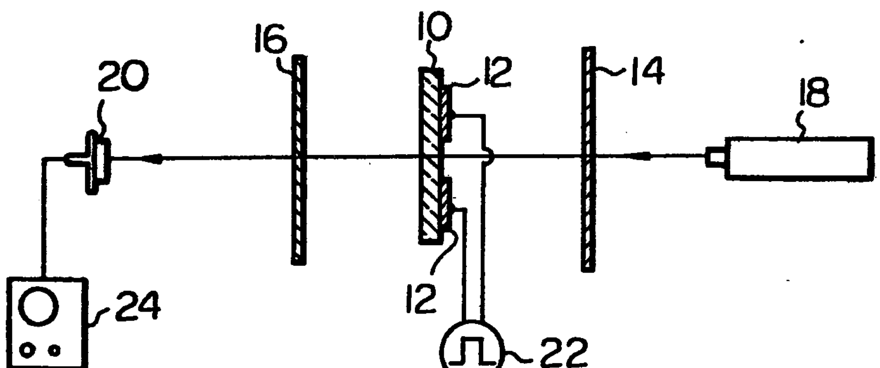

Li
Sr
Aℓ
400
300
200
100
0
CURIE POINT (°C)
0.5
1
2
3
5
10
x: TOTAL OF ELEMENTS A AND B
$(Pb_{1-x}La_{x/2}B_{x/2})(Zr_{0.65}Ti_{0.35})_{1-\frac{x}{4}}O_3$

Fig. 6



SPECIFICATION

Electrooptic ceramic material

This invention relates to a transparent and electrooptic ferroelectric ceramic material.

In general the electrooptic effect is described as follows.

When an electric field is applied to a medium for light, the refraction index n of the medium can be approximated by the following equation:

$$\Delta\left(\frac{1}{n^2}\right)=f\cdot E+h\cdot E^2 \qquad (1)$$

where E is the strength of the electric field. On the right side of the equation, the first term represents linear electrooptic effect (Pockets effect) and the second term does quadratic electrooptic effect;

Principally, practical applications of the electrooptic effect are classified into two categories. In one category, birefringence is controlled electrically, and in the other category scattering of light is controlled electrically.

At present a variety of applications of the electroopic effect are under development, mostly using transparent and ferroelectric ceramics. Some examples are electrooptical valves, electrooptical shutters, electrooptical memories, image storage devices, display devices and polarizers.

As a typical example of devices embodying electrical control of birefringence, an electrooptical valve is constructed and operates as follows.

A principal element of this device is a plate of a transparent and ferroelectric ceramic, and a pair of electrodes are disposed with a definite distance therebetween on one side of the ceramic plate. A linear polarizer is arranged in front of the ceramic plate, and another linear polarizer is positioned in the rear of the ceramic plate so as to have its polarization axis at an angle of 90° to that of the front polarizer (crossed nicol arrangement). The electrodes are arranged such that the direction of an electric field produced on the surface of the ceramic plate by application of a voltage to the electrodes is at an angle of 45° to the polarization planes. When a predetermined voltage is applied to the electrodes while polarized light passes through the ceramic plate, the intensity of light emerging from the device varies according to Equation (2) due to a phase difference developed by the electric field.

$$I_{out}=I_{in}\sin^2\left(\frac{\Gamma\pi}{\lambda}\right) \qquad (2)$$

where I_{out} and I_{in} represent the emerging light and incident light, respectively, Γ is retardation in the ceramic plate, and λ is wavelength. The emerging light I_{out} minimizes when the retardation is an integral multiple of λ, i.e. $\Gamma=n\lambda$, and maximizes when $\Gamma=(n-1/2)\lambda$. Accordingly this device can be operated as an electrooptical valve by controlling the polarizing condition so as to vary within the range from a value corresponding to $\lambda/2$ to another value corresponding to λ. The same device can be operated as an electrooptical shutter by allowing Γ to alternately take two values respectively corresponding to $\lambda/2$ and λ.

In cases where light scattering effect is utilized, transparent electrodes are attached to both sides of a plate of a transparent and ferroelectric ceramic, and a constant voltage is applied to the electrodes to cause a phase shift and, hence, scattering of light thereby to control transmittance of the light. A promising application of this technique is new types of image display devices.

Ferroelectric materials such as KH_2PO_4 (KDP), $KH_4H_2PO_4$ (ADP), $LiNbO_3$ and $Ba_2NaNb_5O_{15}$ are well known as electrooptic materials. These materials are of use only in the form of single crystals, but it is difficult to produce large-sized single crystals of these materials with good quality.

A recently developed electrooptic ferroelectric materials is a lead lanthanum zirconate titanate solid solution obtained by lanthanum substitution for lead in the familiar lead zirconate titanate system $Pb(Zr, Ti)O_3$. The lanthanum substituted system is commonly referred to as PLZT. As a matter of convenience in practical applications, PLZT ceramics are of use in the form of polycrystals and can be produced in large sizes (e.g. cylinders or discs more than 10 cm in cross-sectional area) by hot-pressing, i.e. by compacting calcined particles of a ceramic composition inot a desired shape and sintering the shaped composition in an oxygen atmosphere at a temperature of about 1000—1300°C for about 10—30 hr at a pressure of about 100—300 kg/cm² by the use of an appropriate hot-pressing apparatus. The products are transparent and pale yellowish ceramics.

Advantageously, PLZT ceramics are high in optical transmittance and exhibit quick response to changes in electric field. However, there are some problems such as difficulties in using PLZT ceramics in certain fields exemplified by image display devices because of complication of driving circuits attributed to relatively high polarizing field strength (driving voltage) required for the utilization of this material and the need of continuing high temperature sintering for a long period of time in the production of this material. Nevertheless, transparent and electrooptic ferroelectric ceramics are greatly

expected as the most advantageous material in a large field of optoelectronics.

It is an object of the present invention to provide a transparent ferroelectric ceramic material which exhibits a good electrooptic effect and can be produced easily.

Essentially, a transparent and electrooptic ferrolectric ceramic material according to the invention has the composition

$$(Pb_{1-x}A_aB_b)(Zr_yTi_{1-y})_{1-\frac{x}{4}}O_3,$$

where A represents a rare earth element, B represents an element selected from Group I, II and III elements, $0.004 \leq x \leq 0.15$, $0.6 \leq y \leq 0.8$, $a+b=x$, $a \neq 0$ and $b \neq 0$.

Preferably the element A is selected from Nd, Sm, Eu, Gd and La, and the element B is selected from Li, Na, K, Mg, Sr, Ba and Al.

A ceramic material according to the invention can be produced by hot-pressing fundamentally similarly to known PLZT ceramics, but the hot-pressing can be achieved at a relatively low temperature and completed in a relatively short period of time.

Fig. 1 is a graph showing the spectral transmittance characteristic of an electrooptic ceramic of the invention with respect to an exemplary composition;

Figs. 2 and 3 are two typical examples of hysteresis curves of electrical polarization versus applied electric field for electrooptic ceramics according to the invention;

Figs. 4 and 5 are graphs showing variations in the Curie point of electrooptic ceramics according to the invention with changes in the kinds and amounts of the elements A and B; and

Fig. 6 shows diagrammatically an experimental apparatus for examining the function of an electrooptical shutter utilizing an electrooptic ceramic material.

As described hereinbefore, the present invention provides electrooptic ceramics generally of the composition

$$(Pb_{1-x}A_aB_b)(Zr_yTi_{1-y})_{1-\frac{x}{4}}O_3, \quad (3)$$

where A and B represent substituted elements as defined hereinbefore.

In the production of these ceramics, PbO, ZrO_2 and TiO_2 are used as raw materials for the fundamental components of the ceramics, and selected substitution elements are introduced in the form of either oxide or carbonate into a fundamental composition. At first, the raw material in powder form are individually weighed in accordance with the formula (3). By way of example, Table 1 shows the amounts of the raw materials to be weighed when the elements A and B are respectively neodymium Nd and lithium Li, $a=b=x/2$, and $y=0.65$.

TABLE 1

Symbol	Pb	A	B	Zr	Ti
Raw Material	PbO (g)	Nd_2O_3 (g)	Li_2CO_3 (g)	ZrO_2 (g)	TiO_2 (g)
x = 0.01	221.0	1.683	0.369	79.84	27.88
x = 0.02	218.7	3.365	0.739	79.68	27.83
x = 0.04	214.3	6.730	1.478	79.28	27.69
x = 0.05	212.0	8.411	1.852	79.08	27.62
x = 0.07	207.6	11.78	2.591	78.68	27.48
x = 0.09	203.1	15.14	3.334	78.28	27.34
x = 0.10	200.9	16.82	3.690	78.08	27.27
x = 0.12	196.4	20.19	4.431	77.68	27.17
x = 0.14	192.0	23.55	5.170	77.28	26.99
x = 0.15	189.7	25.24	5.542	77.12	26.93
x = 0.20	178.6	33.65	7.389	76.08	26.57

A typical process of producing an electrooptic ceramic material according to the invention comprises the following steps.

(1) Weighing: powdery materials are weighed in appropriate amounts as demonstrated above.

(2) Grinding-Mixing: the weighed raw materials are ground in a mortar or a ball to accomplish thorough mixing.

(3) Calcining: the powder mixture is placed in an aluminum boat and calcined in an electric furnace at about 900°C for about 1 hr.

(4) Grinding: the calcined mixture is further ground with the addition of deionized water, followed by drying.

(5) Press-forming: the calcined and ground mixture was die-formed into a desired shape such as a disc by the application of a pressure of about 500 kg/cm^2 at room temperature.

(6) Hot-pressing: placed in the die and with continued application of a pressure of about 100—300 kg/cm^2, the shaped material is sintered in an oxygen atmosphere for about 5—15 hr at a temperature between about 900 and 1300°C. A preferred die material is high purity aluminum, and the ceramic material under treatment is enclosed in a filler which is preferably ZrO_2.

(7) Polishing: both sides of the hot-pressed ceramic disc are mirror-finished by rubbing and buffing.

In the ceramic composition expressed by the formula (3), when b=0, the element A (rare earth element) contributes particularly to the improvement of the D (electric polarization)—E (applied voltage) hysteresis characteristic of the ceramic.
When a=0, the element B (a Group I, II or III element) contributes particularly to the improvement of the optical transmittance of the ceramic. When a$\neq$0 and B$\neq$0 as specified above, the substitution according to the invention produces joint effects of the elements A and B.

It was confirmed that neodymium Nd, samarium Sm, europium Eu, gadolinium Gd and lanthanum La are most effective and practical among rare earth elements. When the element A is selected from these five elements, it is preferable that the element B is Li, Na, K, Mg, Sr, Ba or Al.

With respect to thirty five different combinations of the preferred rare earth elements and the preferred Group I, II or III elements, Tables 2—(i), 2—(ii) and 2—(iii) present the results of a series of experiments carried out to examine D—E hysteresis curves and optical transmittance of the ceramics of the formula (3), where x was varied, y was constantly 0.65, and constantly a=b=x/2. The samples in the experiments were ceramic discs produced by the above described process with aluminum electrodes disposed on the mirror-finished surfaces by vacuum evaporation.

As to optical transmittance, use was made of samples 200 μm thick, and transmittance was measured over the visible and near ultrared regions. The symbols A, B, C and X in the transmittance columns of the Tables indicate the results as follows.

A : more than 60% transmittance.
B : 30 to 60% transmittance.
C : less than 30% transmittance, but transparent.
X : only a few percent transmittance and opaque,

As to D—E hysteresis curves, the symbols A, B, C, X, (W) and (S) in the Tables indicate the results as follows.

A : exhibited a remarkable hysteresis, i.e. D>20 μc/cm^2.
B : D was 10 to 20 μc/cm^2.
C : D was 5 to 10 μc/cm^2.
X:D was smaller than 5 μ/cm^2.
(W) : wide-type hysteresis curves as shown in Fig. 2.
(S) : Slim-type hysteresis curves as shown in Fig. 3.

The samples marked by the symbol X either in transmittance or hysteresis were judged to be impractical, and the other samples were judged to be practically of use.

These experiments were carried out with a constant Zr/Ti ratio of 65/35, but nearly similar results were obtained when this ratio was varied within the range between 80/20 and 60/40.

TABLE 2 — (I) $(Pb_{1-x}A_{x/2}B_{x/2})(Zr_{0.65}Ti_{35})_{1-\frac{x}{4}}O_3$

		Element B														
		Li (Li_2CO_3)					Na (Na_2CO_3)					K (K_2CO_3)				
		x = a + b					x = a + b					x = a + b				
Element A		0.01	0.04	0.10	0.15	0.20	0.01	0.04	0.10	0.15	0.20	0.01	0.04	0.10	0.15	0.20
Nd (Nd_2O_3)	Transmittance	C	A	A	A	C	C	A	A	A	C	X	B	B	B	C
	D–E Hysteresis	C	B (W)	A (S)	A (S)	X	X	B (W)	B (S)	B (S)	C	X	C (W)	A (W)	B (W)	X
Sm (Sm_2O_3)	Transmittance	X	C	C	C	X	C	B	B	B	C	X	C	C	C	X
	D–E Hysteresis	X	B (W)	B (W)	B (W)	X	X	C (W)	B (W)	C (W)	X	X	B (W)	B (W)	B (W)	C
Eu (Eu_2O_3)	Transmittance	C	B	A	B	X	X	B	A	B	X	X	C	B	B	X
	D–E Hysteresis	C	B (W)	A (W)	B (W)	X	B	A (W)	B (W)	C (W)	X	C	B (W)	B (W)	B (W)	C
Gd (Gd_2O_3)	Transmittance	C	B	B	C	X	X	C	C	C	X	X	C	C	C	X
	D–E Hysteresis	X	C (W)	B (W)	B (W)	X	X	C	B (W)	B (W)	C	C	C	C	C	X
La (La_2O_3)	Transmittance	X	B	B	B	X	X	C	A	A	C	X	C	A	A	C
	D–E Hysteresis	B (W)	B (W)	B (S)	B (S)	C (S)	C (W)	B (W)	A (S)	B (S)	X	C (W)	B (W)	A (S)	B (S)	X

TABLE 2 – (II) $(Pb_{1-x}A_{x/2}B_{x/2})(Zr_{0.65}Ti_{0.35})_{1-\frac{x}{4}}O_3$

		Element B														
		Mg (MgO)					Sr (SrO)					Ba (BaO)				
		x = a + b					x = a + b					x = a + b				
Element A		0.01	0.04	0.10	0.15	0.20	0.01	0.04	0.10	0.15	0.20	0.01	0.04	0.10	0.15	0.20
Nd . (Nd_2O_3)	Transmittance	X	C	B	B	X	X	C	B	B	X	X	C	B	B	X
	D–E hysteresis	X	C	A (W)	B (W)	X	C	B	A	B	X	X	B	A	B	X
Sm . (Sm_2O_3)	Transmittance	C	B	B	X	X	C	C	C	X	X	X	C	B	B	X
	D–E Hysteresis	X	X	X	C	X	X	B	A	B	X	C	B	A	B	C
Eu . (Eu_2O_3)	Transmittance	X	X	X	X	X	C	C	B	B	X	X	C	C	C	X
	D–E Hysteresis	X	C	C	C	X	X	B	B	C	C	B	A	A	B	X
Gd . (Gd_2O_3)	Transmittance	X	C	C	X	X	X	C	C	C	X	X	C	C	C	X
	D–E Hysteresis	X	X	C	X	X	X	B	B	B	C	C	B	B	B	C
La . (La_2O_3)	Transmittance	X	C	C	X	X	C	A	A	A	X	C	C	B	B	X
	D–E Hysteresis	X	X	X	X	X	C	B (W)	A (S)	A (S)	C	C	B (W)	A (S)	A (S)	C

TABLE 2 – (III)

$$(Pb_{1-x}A_{x/2}B_{x/2})(Zr_{0.65}Ti_{0.35})_{1-\frac{x}{4}}O_3$$

		Element B				
		Al (Al_2O_3)				
		x = a + b				
Element A		0.01	0.04	0.10	0.15	0.20
Nd (Nd_2O_3)	Transmittance	C	C	B	B	X
	D–E Hysteresis	X	B	B	B	X
Sm (Sm_2O_3)	Transmittance	X	C	C	X	X
	D–E Hysteresis	C	B	A	B	X
Eu (Eu_2O_3)	Transmittance	X	C	C	X	X
	D–E Hysteresis	C	B	A	B	X
Gd (Gd_2O_3)	Transmittance	C	C	C	C	X
	D–E Hysteresis	C	B	A	B	C
La (La_2O_3)	Transmittance	X	C	A	A	C
	D–E Hysteresis	C	A (W)	A (S)	B (S)	C

The following conclusions could be deduced from the experimental results summarized in the above Tables and the results of other experiments.

When the element A is Nd, the use of a Group I element (selected from Li, Na and K) as the element B gives an electrooptic ceramic excellent both in transparency and relative permitivity: the best results can be obtained by using Li or Na, and the use of K follows it. The Group II elements (Mg, Sr, Ba) are effective next to the Group I elements and follows the Group II elements (A1).

When Sm, Eu or Gd is employed as the element A, the Group I elements are the most suitable as the element B. In this case there is little difference between the Groups II and III elements except that Mg is lower in effect than the others.

When the element A is La, the use of Sr, Ba or Al as the element B is the most favorable although the use of Na, K or Li, too, gives a good electrooptic ceramic. In this case Mg is considerably lower in effect.

Fig. 1 shows spectral transmittance of $(Pb_{0.9}Nd_{0.05}Li_{0.05})(Zr_{0.65}Ti_{0.35})_{0.975}O_3$, a typical example of electrooptic ceramics according the invention. Among the ceramics of the invention, those comprising Nd are characterized by their pale blue color.

In the ceramics according to the invention, the Curie point depends on the kinds and amounts of the substituted elements A and B. Fig. 4 shows variations in the Curie point when the element A is Nd and the element B is Li, Na or K. Fig. 5 shows variations in the Curie point when the element A is La and the element B is Li, Sr or Al. In the experiments that gave the curves of Figs. 4 and 5, the atomic ratio of the element A to the element B was made constantly 1:1, and the ratio Zr:Ti was 65:35.

Changes in the Curie point are closely related to changes in crystal structure of the tested materials. When the Curie point of a material is as low as room temperature, this material readily exhibits a change in its crystal structure upon application of an electric field thereto at room temperature.

Among transparent and electrooptic ceramics according to the invention, those exhibiting wide-type hysteresis curves as shown in Fig. 2 have memory capabilities and accordingly will be of use, for example, in the field of image display. The ceramics exhibiting slim-type hysteresis curves as shown in Fig. 3 have an instantaneous light extinction capability and accordingly will be of use for optical shutters and optical valves.

Fig. 6 shows an experimental apparatus to examine an optical shutter effect of a transparent and electrooptic ceramic according to the invention of the composition $(Pb_{0.9}Nd_{0.05}Li_{0.005})(Zr_{0.65}Ti_{0.35})_{0.965}O_3$.

In Fig. 6, reference numeral 10 indicates a plate of this ceramic material. A pair of aluminum electrodes 12 were formed on one side of the ceramic plate 10 by vacuum evaporation in a parallel arrangement with a distance of 0.5 mm therebetween. Two polarizers 14 and 16 were arranged in the crossed nicol orientation so as to interpose the ceramic plate 10 therebetween. A He-Ne laser device 18 and a phototransistor 20 were positioned such that a laser light beam passed through the polarizers 14, 16 and the transparent ceramic plate 10 arrived at the phototransistor 20. To control the transmission of the laser light through the ceramic plate 10, a DC voltage was applied to the electrodes 12 by the use of a pulse generator 22, and resulting changes in the transmissitivity of the ceramic plate 10 were measured by connecting the phototransistor 20 to a memory-type oscilloscope 24. When a pulse-like voltage of 400 V was applied to the electrodes 12, the transmissivity of the ceramic plate 10 became more than 90% in a few microseconds. Upon interruption of the application of the voltage, the transmissivity became less than 10% in a few microseconds. Thus it was confirmed that the testing ceramic material is useful in producing optical shutters of very quick responsiveness.

The merits of the present invention are summarized as follows.

(1) The invention provides ferroelectric ceramics which exhibit remarkable electrooptic effect and are very high in transparency.

(2) The ceramics according to the invention can easily be produced by a known hot-pressing method, and it is possible to accomplish hot-pressing at a reduced temperature and in a shortened period of time compared with hot-pressing of conventional PLZT ceramics.

(3) The ceramics according to the invention exhibit electrooptic effect by the application of an electric field of a relatively low strength, so that a driving circuit of a relatively small capacity suffices for an electrooptical device utilizing a ceramic according to the invention.

CLAIMS

1. An electrooptic ferroelectric ceramic material consisting essentially of a ceramic expressed by the formula

$$(Pb_{1-x}A_aB_b)(Zr_yTi_{1-y})_{1-\frac{x}{4}}O_3,$$

where A represents a rare earth element, B represents an element selected from Groups I, II and III elements, $0.04 \leq x \leq 0.15$, $0.6 \leq y \leq 0.8$, $a+b=x$, $a \neq 0$ and $b \neq 0$.

2. An electrooptic ferroelectric ceramic material according to Claim 1, wherein the element A is selected from Nd, Sm, Eu, Gd and La, the element B being selected from Li, Na, K, Mg, Sr, Ba and Al.

3. An electrooptic ferroelectric ceramic material according to Claim 1, wherein the element A is Nd, the element B being selected from Li, Na, K, Mg, Sr and Ba.

4. An electrooptic ferroelectric ceramic material according to Claim 1, wherein the element A is selected from Sm, Eu and Gd, the element B being selected from Li, Na, Sr, Ba and Al.

5. An electrooptic ferroelectric ceramic material according to Claim 1, wherein the element A is La, the element B being selected from Na, K, Sr, Ba and Al.

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